EARLY ENTRANCE COPRODUCTION PLANT

PHASE II

Topical Report

Task 3.0: **Update and Implement Additional Research, Development, and Testing**
Secondary Fischer-Tropsch Catalyst/Wax Separation with Micro-filtration

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Contributors: John Anderson (ChevronTexaco)
Mark Anselmo (Rentech)
Earl Berry (ChevronTexaco)
Mark Bohn (Rentech)
Ming He (ChevronTexaco)
Charles H. Schrader (ChevronTexaco)
Lalit Shah (ChevronTexaco)
Donald Todd (LCI)
Robert Schavey (LCI)

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Texaco Energy Systems LLC
3901 Briarpark Drive
Houston, Texas 77042

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Abstract

The overall objective of this project is the three phase development of an Early Entrance Coproduction Plant (EECP) which uses petroleum coke to produce at least one product from at least two of the following three categories: (1) electric power (or heat), (2) fuels, and (3) chemicals using ChevronTexaco's proprietary gasification technology. The objective of Phase I is to determine the feasibility and define the concept for the EECP located at a specific site; develop a Research, Development, and Testing (RD&T) Plan to mitigate technical risks and barriers; and prepare a Preliminary Project Financing Plan. The objective of Phase II is to implement the work as outlined in the Phase I RD&T Plan to enhance the development and commercial acceptance of coproduction technology. The objective of Phase III is to develop an engineering design package and a financing and testing plan for an EECP located at a specific site.

The project's intended result is to provide the necessary technical, economic, and environmental information needed by industry to move the EECP forward to its detailed design, construction, and operation. The partners in this project are Texaco Energy Systems LLC (TES) (a subsidiary of ChevronTexaco), General Electric (GE), Praxair, and Kellogg Brown & Root (KBR). The work was under cooperative agreements with the U.S. Department of Energy (DOE). TES is providing the gasification technology and the Fischer-Tropsch (F-T) technology developed by Rentech Inc., GE is providing the combustion turbine technology, Praxair is providing the air separation technology, and KBR is providing overall engineering.

Each of the EECP's subsystems was assessed for technical risks and barriers in Phase I. A plan was identified to mitigate the identified risks (Phase II RD&T Plan, October 2000). The RD&T Plan identified catalyst/wax separation as a potential technical and economic risk. To mitigate risks to the proposed EECP concept, Phase II RD&T included tests for secondary catalyst/wax separation systems as part of Task 2.3 – Catalyst/Wax Separation. The LCI Scepter® Micro-filtration system was determined to be best suited for producing a filtrate that met the EECP secondary catalyst/wax separation standards of producing F-T wax containing less than10 ppmw solids. As part of task 2.3, micro-filtration removal efficiencies and production rates for two F-T feeds, Rentech Inc. bubble column reactor (BCR) product and LaPorte Alternative Fuels Development Unit (AFDU) product, were evaluated. Based on comparisons between the performances of these two materials, the more readily available LaPorte AFDU material was judged an acceptable analog to the BCR material that would be produced in a larger-scale F-T synthesis. The present test was initiated to obtain data in an extended range of concentration for use in the scale-up design of the secondary catalyst/wax separation system that would be operating at the EECP capacity.

Table of Contents

List of Graphical Material

Figures

Schematics

Table

Executive Summary

The overall objective of this project is the three phase development of an Early Entrance Coproduction Plant (EECP) which uses petroleum coke to produce at least one product from at least two of the following three categories: (1) electric power (or heat), (2) fuels, and (3) chemicals using ChevronTexaco's proprietary gasification technology. The objective of Phase I was to determine the feasibility and define the concept for the EECP located at a specific site; develop a Research, Development, and Testing (RD&T) Plan for implementation in Phase II; and prepare a Preliminary Project Financing Plan. The objective of Phase II is to perform RD&T to enhance the development and commercial acceptance of coproduction technology. The objective of Phase III is to develop an engineering design package and a financing and testing plan for an EECP located at a specific site. The project's intended result is to provide the necessary technical, economic, and environmental information needed by industry to move the EECP forward to the detailed design, construction, and operation.

Each of the EECP subsystems was assessed for technical risks and barriers. A plan was identified to mitigate the identified risks (Phase II RD&T Plan, October 2000). Catalyst/Wax Separation was identified as one of the most important technical risks of the Fischer-Tropsch (F-T) Synthesis Unit. There are two main purposes for the Catalyst/Wax Separation system. The first purpose is to keep the catalyst inventory in the reactor. If the separation system does not work properly, then the reactor will lose catalyst in the product filtrate. The second purpose is to clean up the solids from the Heavy F-T liquid product before processing it in the F-T Product Upgrading Unit. Catalyst/wax separation represents a high economic risk to the EECP. To ensure product value, the solids in the Heavy F-T liquid product must be reduced to at least 10 parts-per-million (weight) [ppmw]. Currently, the design for the catalyst/wax separation system is split it into two stages: the Primary Separation Stage and the Secondary Separation Stage. The primary separation must be able to fulfill the first purpose of maintaining the catalyst inventory within the reactor. Its objective is to perform the bulk separation by removing a filtrate stream with less than 0.5 weight percent (wt %) solids from a slurry containing 20+ wt% solids and returning all the catalyst back to the reactor. The second stage catalyst/wax separation system will remove the remaining catalyst solids from the filtrate before sending to the F-T Product Upgrading. The objective of the second stage catalyst/wax separation system is to reduce the filtrate or wax solids content from 0.5 wt% to ~10 ppmw.

To mitigate risks to the proposed EECP, Phase II RD&T included tests for secondary catalyst/wax separation systems as part of Task 2.3 – Catalyst/Wax Separation. The LCI Scepter® Micro-filtration system was determined to be best suited for producing a filtrate that met the EECP secondary catalyst/wax separation standards of producing filtrate with solids content of less than 10 ppmw. As part of Task 2.3, in previous tests, micro-filtration removal efficiencies and production rates for two feeds - Rentech bubble column reactor (BCR) and the LaPorte Alternative Fuels Development Unit (AFDU) were evaluated. Based on comparisons between performances of these two materials, the more readily available LaPorte AFDU material was judged to be an acceptable analog to the BCR material that would be produced in a larger-scale F-T synthesis. The present test was initiated to obtain data in an extended range of concentration for use in the scale-up design of the secondary catalyst/wax separation system operating at EECP capacity.

Background

The overall objective of this project is the three phase development of an EECP which uses petroleum coke to produce at least one product from at least two of the following three categories: (1) electric power (or heat), (2) fuels, and (3) chemicals. The objective of Phase I was to determine the feasibility and define the concept for the EECP located at a specific site; develop a Research, Development, and Testing (RD&T) Plan for implementation in Phase II; and prepare a Preliminary Project Financing Plan. The objective of Phase II is to implement the work as outlined in the Phase I RD&T Plan to enhance the development and commercial acceptance of coproduction technology. The objective of Phase III is to develop an engineering design package and a financing and testing plan for an EECP located at a specific site. The project's intended result is to provide the necessary technical, economic, and environmental information needed by industry to move the EECP forward to detailed design, construction, and operation.

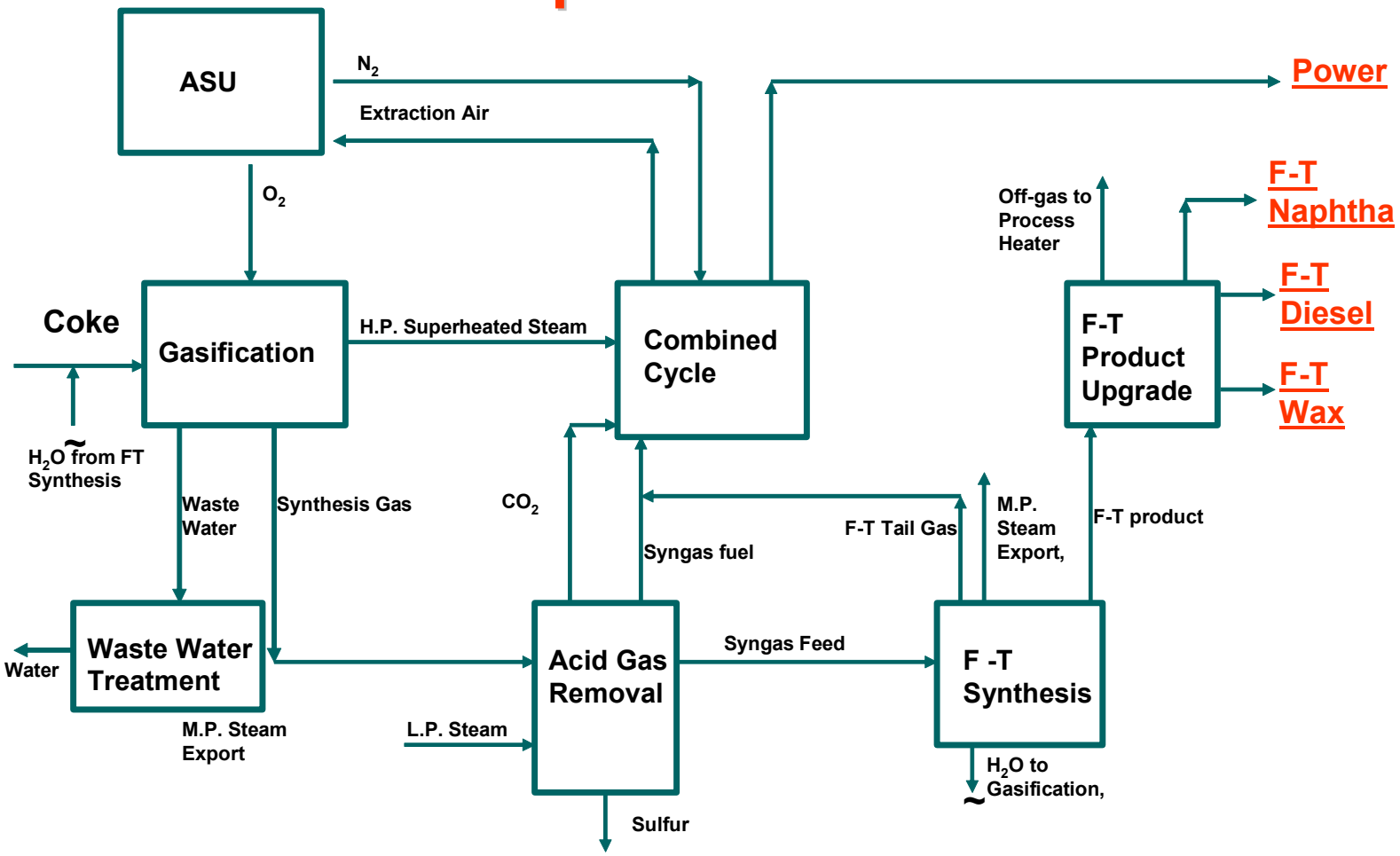
The proposed EECP facility was designed to coproduce electric power and steam for export and internal consumption, finished high-melt wax, finished low-melt wax, F-T diesel, F-T naphtha, elemental sulfur, and consume approximately 1,120 metric tons per day (1,235 short tons per day) of petroleum coke. During Phase I, the Motiva Port Arthur Refinery site was chosen for the EECP. The refinery site offered a ready source of petroleum coke as a feedstock.

EECP Concept

As shown in **Schematic 1**, petroleum coke is ground, mixed with water and pumped as thick slurry to the Gasification Unit. This coke slurry is mixed with high-pressure oxygen from the Air Separation Unit (ASU) and a small quantity of high-pressure steam in a specially designed feed injector mounted on the gasifier. The resulting reactions take place very rapidly to produce synthesis gas, also known as syngas, which is composed primarily of hydrogen (H_2), carbon monoxide (CO), water vapor (H_2O), and carbon dioxide (CO_2) with small amounts of hydrogen sulfide (H_2S), methane, argon, nitrogen, and carbonyl sulfide. The raw syngas is scrubbed with water to remove solids, cooled, and then forwarded to the Acid Gas Removal Unit (AGR), where the stream is split. One portion of the stream is treated in the AGR to remove CO_2 and H_2S and then forwarded to the F-T Synthesis Unit. The other portion is treated in the AGR to remove the bulk of H_2S with minimal CO_2 removal and then forwarded as fuel to the GE frame 6FA gas turbine. In the AGR solvent regeneration step, high pressure nitrogen from the ASU is used as a stripping agent to release CO_2. The resulting CO_2 and nitrogen mixture is also sent to the gas turbine, which results in increased power production and reduced nitrogen oxides emissions. The bulk of the nitrogen is also sent to the gas turbine as a separate stream, where its mass flow also helps increase the power production and reduces nitrogen oxides emissions.

Overall, approximately 75% of the sweetened syngas is sent to the gas turbine as fuel. The remaining 25% is first passed through a zinc oxide bed arrangement to remove the remaining traces of sulfur and then forwarded to the Fischer-Tropsch (F-T) Synthesis Unit. In the F-T

Proposed EECP



Schematic 1 – EECP Concept

reactor, carbon monoxide (CO) and hydrogen (H_2) react, aided by an iron-based catalyst, to form mainly heavy straight-chain hydrocarbons. Since the reactions are highly exothermic, cooling coils are placed inside the reactor to remove the heat released by the reactions. Three hydrocarbon product streams, heavy F-T liquid, medium F-T liquid, and light F-T liquid are sent to the F-T Product Upgrading unit while F-T water, a reaction byproduct, is returned to the Gasification Unit and injected into the gasifier either directly or through the use in slurry preparation area of Gasification Unit. The F-T tail gas and AGR off gas are sent to the gas turbine as fuel to increase electrical power production by 11%.

In the F-T Product Upgrading Unit (F-TPU), the three F-T liquids are combined and processed as a single feed. In the presence of a hydrotreating catalyst, hydrogen (H_2) reacts slightly exothermally with the feed to produce saturated hydrocarbons, water, and some hydrocracked light ends. The resulting four liquid product streams are naphtha, diesel, low-melt wax, and high-melt wax and leave the EECP facility via tank truck.

The power block consists of a GE PG6101 (6FA) 60 Hertz (Hz) heavy-duty gas turbine generator and is integrated with a two-pressure level heat recovery steam generator (HRSG) and a non-condensing steam turbine generator. The system is designed to supply a portion of the compressed air feed to the ASU, process steam to the refinery, and electrical power for export and use within the EECP facility. The gas turbine has a dual fuel supply system with natural gas as the start-up and backup fuel, and a mixture of syngas from the gasifier, off gas from the AGR Unit, and tail gas from the F-T Synthesis Unit, as the primary fuel. Nitrogen gas for injection is supplied by the ASU for nitrous oxide (NOx) abatement, power augmentation, and the fuel purge system.

The Praxair ASU is designed as a single train elevated pressure unit. Its primary duty is to provide oxygen to the gasifier and Sulfur Recovery Unit (SRU), and all of the EECP's requirements for nitrogen and instrument and compressed air. ASU nitrogen product applications within the EECP include its use as a stripping agent in the AGR Unit, as diluents in the gas turbine where its mass flow helps increase power production and reduce NOx emissions, and as an inert gas for purging and blanketing. The gas turbine, in return for diluents nitrogen, supplies approximately 25% of the air feed to the ASU, which helps reduce the size of the ASU's air compressor, hence oxygen supply cost.

Acid gases from the AGR, as well as sour water stripper (SWS) off gas from the Gasification Unit, are first routed to knockout drums as they enter the Claus SRU. After entrained liquid is removed in these drums, the acid gas is preheated and fed along with the SWS gas, oxygen, and air to a burner. In the thermal reactor, the H_2S, a portion of which has been combusted to sulfur dioxide (SO_2), starts to recombine with the SO_2 to form elemental sulfur. The reaction mixture then passes through a boiler to remove heat while generating steam. The sulfur-laden gas is sent to the first pass of the primary sulfur condenser in which all sulfur is condensed. The gas is next preheated before entering the first catalytic bed in which more H_2S and SO_2 are converted to sulfur. The sulfur is removed in the second pass of the primary sulfur condenser, and the gas goes through a reheat, catalytic reaction, and condensing stage two more times before leaving the

SRU as a tail gas. The molten sulfur from all four condensing stages is sent to the sulfur pit, from which product is transported off site by tank truck.

The tail gas from the SRU is preheated and reacted with hydrogen in a catalytic reactor to convert unreacted SO_2 back to H_2S. The reactor effluent is cooled while generating steam before entering a quench tower for further cooling. A slip stream of the quench tower bottoms is filtered and sent along with the condensate from the SRU knockout drums to the SWS. H2S is removed from the quenched tail gas in an absorber by lean methyldiethanolamine (MDEA) solvent from the AGR Unit, and the tail gas from the absorber is thermally oxidized and vented to the atmosphere. The rich MDEA solvent returns to the AGR Unit to be regenerated in the stripper.

Catalyst/Wax Separation

Synthesis gas (H_2 and CO) is fed to the F-T Synthesis Slurry Reactor where it reacts in the presence of catalyst to form a mixture of hydrocarbons and water (Refer to **Schematic** 2). The light hydrocarbons, water, and unconverted synthesis gas leave the reactor as a vapor. The heavy hydrocarbon (wax) stays in the reactor as a liquid. The wax is removed to prevent liquid build up in the reactor.

F-T slurry reactors require the separation of product wax from catalyst in order to maintain the catalyst concentration in the reactor and to obtain a product suitable for further processing. Catalyst slurry concentration in the reactor is typically 20 weight %. For some applications the product wax must be filtered to 10 ppmw. It is generally recognized that there is no single separation technology presently available that can reduce the catalyst concentration by this four orders of magnitude.

Catalyst/wax separation removes the F-T liquid wax from the solid catalyst particles/wax slurry. The purpose is to remove clean liquid products from the F-T reactor while maintaining the catalyst inventory within the reactor. The separation may occur inside or outside of the F-T reactor. In the proposed EECP design, the catalyst/wax separation is accomplished in two stages. The first stage removes the liquid products as filtrate while maintaining reactor catalyst inventory. The second stage removes the remaining catalyst solids from the liquid filtrate before it is sent to the F-T Product Upgrading Section. The catalyst solids removed in the second stage catalyst/wax separation can be recycled back to the reactor; however, it is typically disposed off.

Catalyst/wax separation is one of the most important technical risks of the F-T Synthesis Unit. Catalyst/wax separation represents a high economic risk to the EECP. To ensure product value, the solids in the heavy F-T liquid product must be reduced to at least 10 ppmw.

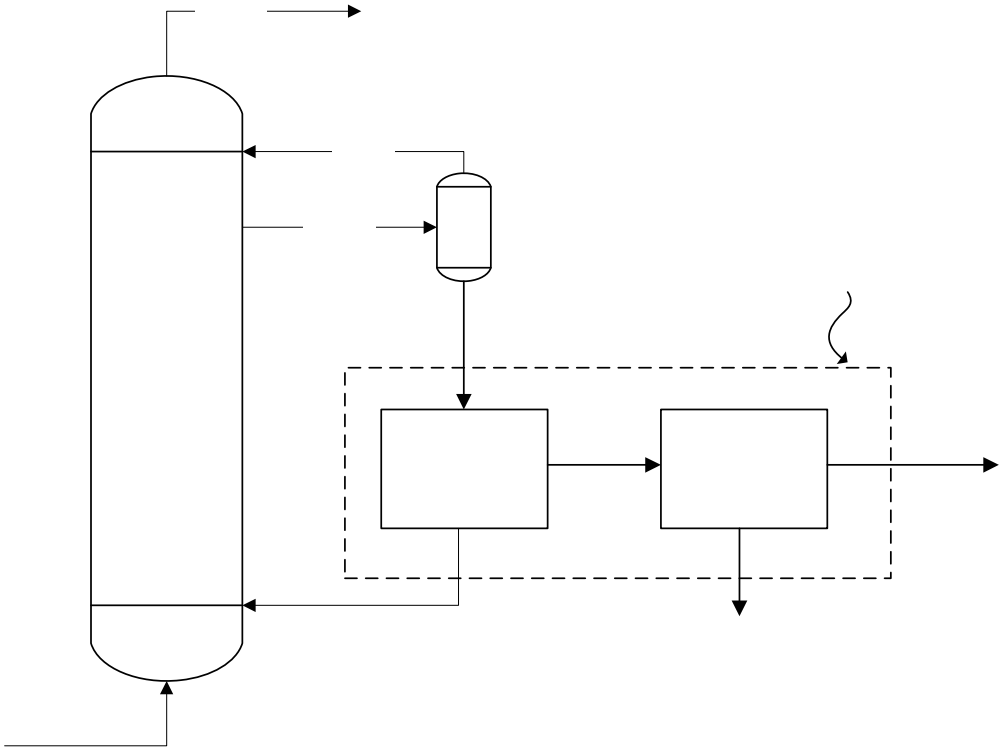
Primary Separation Stage

The primary separation must be able to maintain the catalyst inventory within the reactor. Its objective is to perform the bulk separation by removing a filtrate stream with less than 0.5 weight percent (wt %), preferably 0.1 wt % solids from a 20+ wt% slurry and returning all the catalyst back to the reactor. Please note that once the catalyst leaves the primary separation stage and enters secondary separation stage, this catalyst is removed from the reactor system and is

typically disposed off. To minimize the catalyst loss the primary separation stage filtrate stream solid concentration is preferred to be less than 0.1 weight percent (wt %). As part of Task 2.3, Dynamic Settler was chosen as a primary catalyst/wax separation device.

Secondary Separation Stage

The second stage catalyst/wax separation system removes the remaining catalyst solids from the filtrate before it is sent to the F-T Product Upgrading. The objective is to reduce the solids content from 0.5 wt% to ~10 ppmw. A number of possible methods were identified for accomplishing this task. They included various filtration methods, settling, magnetic separation, electrostatic separation, etc.



Schematic 2 – Catalyst/wax Separation Process Flow Sketch

Rentech and Texaco Energy Systems LLC (TES) screened and tested multiple technologies to meet the EECP secondary catalyst/wax separation system objective of removing the remaining catalyst solids from the filtrate before sending the filtrate to the F-T Product Upgrading. Based on using Rentech primary separation device – Dynamic Settler, the filtrate solids content from the primary catalyst/wax separation system is expected to be less than 0.1 wt %. To account for operation upsets and swings in the secondary catalyst/wax separation feed concentration, a 0.5 to 1 wt % slurry was assumed as a design feed for the secondary catalyst/wax separation. The secondary catalyst/wax separation system must remove the solids to the 10 ppmw level.

As part of Task 2.3 Fischer-Tropsch Catalyst/Wax Separation, several separation technologies were tested for the second stage of the F-T catalyst/wax separation. They included magnetic separation, barrier filtration, and electrostatic separation. Secondary catalyst/wax separation of the F-T liquids is not as trivial as it might appear. The iron catalyst used for Fischer-Tropsch processes in activated form has particles that have typical size distribution from sub microns to the hundreds of microns. The F-T liquids must stay at a high temperature to maintain its low viscosity and not form wax crystals. Since the primary catalyst/wax separation system removes the larger, and easier to remove catalyst particles, the secondary catalyst/wax separation system must remove the smallest particles (sub micron). Attrition in iron-based F-T catalysts slurry operations is well documented (Datye et al., 1996 and Kohler et al., 1994). The F-T slurry feed to the secondary catalyst/wax separation system can have sub microns size particles and can be several orders of magnitude smaller than the starting F-T catalyst size. The sub microns particle size makes the task of producing a 10 ppmw filtrate very difficult. If these sub microns particles are not removed than it could plug the downstream F-T Product Upgrading processes fixed catalyst bed reactors and shorten their on-stream time.

As part of Task 2.3 Fischer-Tropsch Catalyst/Wax Separation the general test plan for all technologies tested was similar. Initial testing was done using the catalyst/oil slurry. If the technology was successful when tested with the catalyst/oil slurry test, a test with catalyst/paraffin wax slurry was conducted. Finally, if that test was successful, the last test would use the actual F-T catalyst/wax slurry. For all the tests, the success of the technology was measured against the required goal of getting the slurry cleaned to 10 ppmw solids.

The catalyst/oil slurry was selected for initial tests since it allowed for a quick screening test at low temperatures (the oil viscosity is approximately the same as the wax viscosity at temperature). This allowed the screening to be done at ambient conditions. Since the amount of F-T catalyst/wax required for most tests exceeded the material TES had available, the paraffin wax/catalyst slurry was used for the next series of tests. The catalyst/paraffin wax test was done at higher temperatures and gave second level of screening which has more realistic parameters than the catalyst/oil test. If any of the technologies passed the above two tests, the final testing would be done with F-T catalyst/wax slurry (Rentech BCR product and/or La Porte AFDU product).

Of the three technologies tested in Task 2.3 Fischer-Tropsch Catalyst/Wax Separation, the LCI Scepter® Micro-filtration system appeared to be the best suited for producing a product filtrate that met the EECP standards of 10 ppmw solids in F-T wax for downstream F-T Product

Upgrading Section. In previous tests as part of Task 2.3: Fischer-Tropsch Catalyst/Wax Separation, LCI and TES evaluated micro-filtration removal efficiencies and production rates for two feeds – Rentech BCR product and La Porte AFDU product.

The Rentech BCR product was made at the Rentech Bubble Column Reactor (BCR) and processed through the Rentech first stage catalyst/wax separation – Dynamic Settler. This slurry represented the slurry with the catalyst size and Fischer-Tropsch wax expected as feed to the second stage of commercial catalyst/wax separation system.

La Porte AFDU product consisted of the La Porte F-T wax/catalyst slurry containing F-T wax and activated catalyst from the AFDU demonstration in LaPorte (done outside DOE funding). The slurry collected at AFDU had 5 to 10 wt% catalyst in the slurry. The AFDU slurry was heated and allowed to settle. The supernatant or lean slurry from the settling operation was used for the above tests.

Based on comparisons between the performances of these two materials, the more readily available LaPorte material was judged as an acceptable analog to the BCR material that would be produced in larger-scale F-T synthesis.

The RD&T done for Task 2.3: Fischer-Tropsch Catalyst/Wax Separation identified a successful technology for producing 10 wppm waxes; however, for a successful implementation of EECP concept, the team felt that additional RD&T was necessary so that a secondary catalyst/wax separation system can be designed for the EECP capacity. The present test was initiated to obtain data in an extended range of concentration for use in the scale-up design of the secondary catalyst/wax separation system operating at EECP capacity.

Objectives

LCI performed tests with the La Porte AFDU catalyst/wax. The objective of the parametric testing was to:

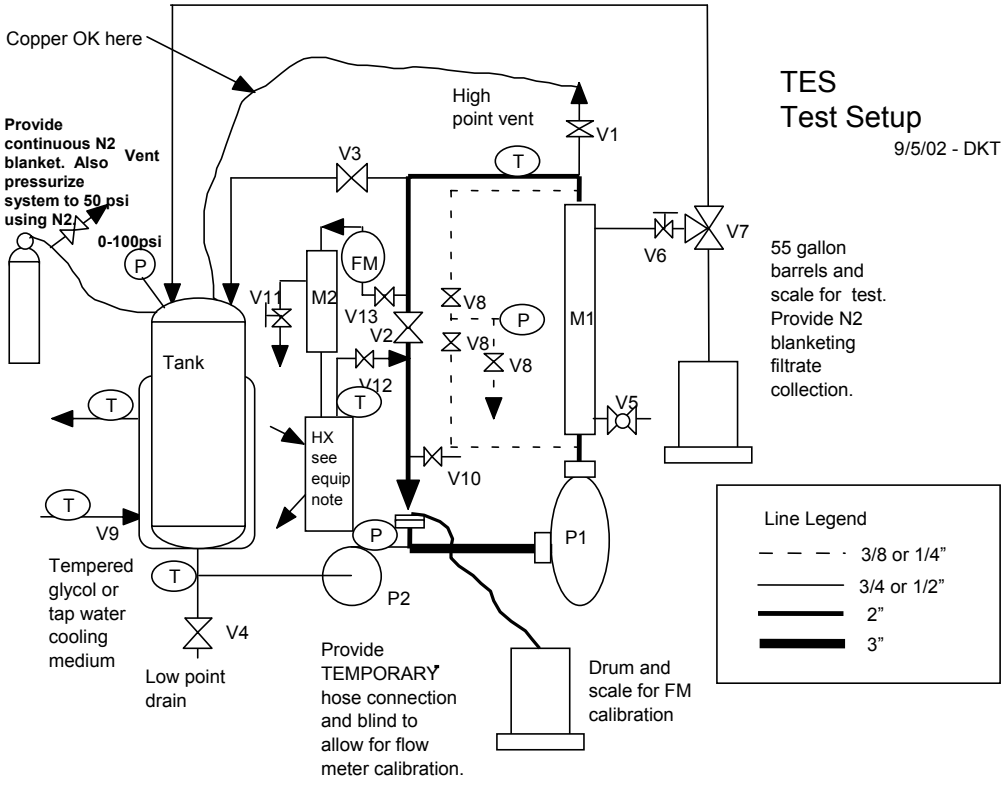
- Generate flux and separation data using new 26 nanometer Scepter filter module.
- Allow comparison of new module data with data from the tests conducted under Task 2.3 (see Topical report Task 2.3: Fischer-Tropsch Catalyst/wax Separation).
- Apply LCI proprietary additive powder to the new Scepter filter surface prior to operation to possibly increase separation efficiency and facilitate cleaning.
- Extend the range of data from approximately 8:1 concentration factor achieved in previous tests done under Task 2.3, to approximately 10:1 in this test series.
- Investigate flux decline over a 24-hour period at low feed slurry concentration.
- Obtain additional operating experience with La Porte AFDU catalyst/wax slurry.
- Obtain additional scale-up data by varying axial fluid velocity at the filtering surface, temperature, and pressure to propose a design for an EECP capacity.
- Test for hysterisis with concentration.

All test objectives were met.

Experimental Set-up

LCI Experimental Set-up is shown in Schematic 3. The experimental set-up was equipped to simultaneously test module M1 and M2 of different capacity. The module M1 (see **Figure 1**) used is a Scepter model 2.5F-750A1-P with 3.77 square feet of filter surface. Module M2 is 1000 Dalton Membralox® module of smaller capacity. A pumping rate of over 100 gallons per minute is available for the Scepter module. Eighty gallons per minute through test module M1 produces 16 feet per second cross-flow velocity in the tubes. The 60-gallon feed tank used is jacketed, and stirred. Heated heat-transfer oil and a 10 square foot heat exchanger supplied heating.

Parametric tests were run in a hot loop designed for a minimum operating volume of 10 gallons or less. Because of the minimum loop volume and the expected volume of feed, the expected concentration factor was between 10:1 and 15:1 (90% to 93% recovery). 94% recovery was actually achieved. Tanks and drums overhead areas were blanketed with nitrogen to minimize atmospheric oxidation of the wax, and the fire hazards. Sample collection areas were not blanketed. The sealed feed tank was pressurized with nitrogen to extend the range of possible trans-membrane operating pressures during portions of the parametric scans.



Schematic 3 – LCI Experimental Set-up

A bypass flow meter configuration was used for this test. A small mass flow meter was placed in parallel with a variable restriction (ball valve) in the flow loop and the system was calibrated using water. The fixed geometry of restriction and the parallel leg set the loop characteristics.

Then the flow-rate that was read on the mass flow meter was then proportional to the total flow in the loop. Flows to and from the feed tank were kept to low levels to minimize error in flow rate readings.

Heat was provided by an electrically heated, Therminol-66 oil system and a 10 square foot, 4-pass heat exchanger system, and through steam tracing. Cooling was provided by ambient convection losses, and by tempered glycol or tempered water flow to a tank jacket when needed.

Filtrate flow rate measurements for determining flux were made using aluminum pans, a balance (0.01 gram precision) and a stop watch. During concentration scans, filtrate was collected in 5-gallon pails or 55-gallon barrels and weighed on a scale. Scale readings was recorded with each measurement.

One hundred fifty milliliter samples of initial feed (from the first barrel), initial filtrate and feed (from the system feed tank) were collected and analyzed for analysis at initial operating conditions, and at selected operating conditions during the test.

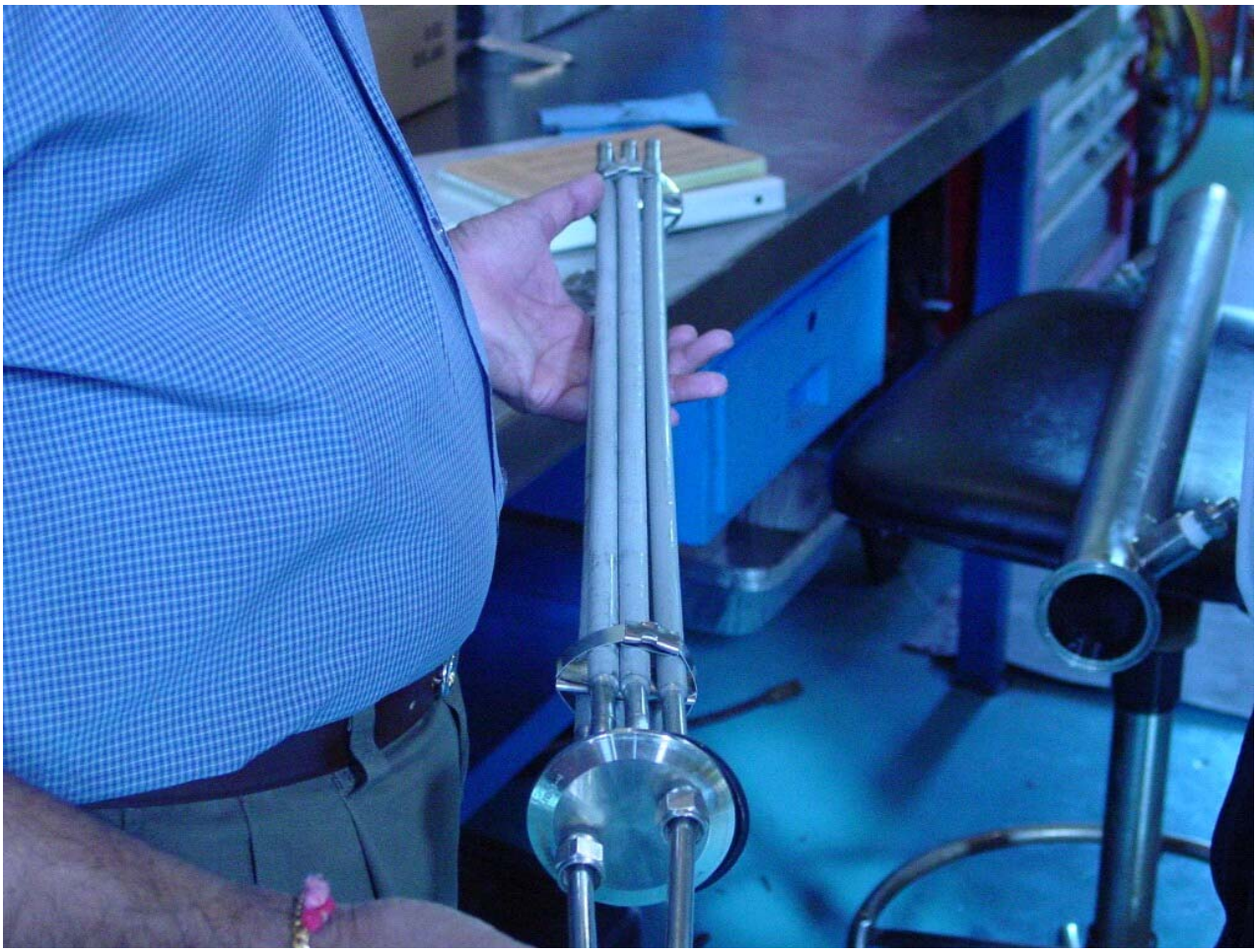


Figure 1. Typical single-pass Scepter® Micro filtration test module
An all-welded module containing several filter tubes in parallel was used in the tests.

Experimental Procedure

The following sequences of operations were performed before parametric testing with La Porte catalyst/wax slurry:

- Calibrate the bypass flow meter in the wax loop system using water and an identical module.
- Rinse the wax loop system with hexane and allow drying overnight using tracing heat.
- Melt catalyst/wax slurry in a steam heated hot box with nitrogen blankets in feed containers overhead areas.
- Add all melted wax to a separate 250 gallon, oil heated tank and mix well.
- Add approximately 390lb. of feed to wax loop stirred feed tank.

Following operations were performed outside the experimental set-up on the new Scepter module Model 2.5F-750A1-P, S/N LCI003, before testing in wax loop:

- Perform a commissioning acid flush.
- Measure baseline flux/pressure ratio (J/P) and bubble point in filtered de-ionized water.
- Add proprietary additive using filtered de-ionized water and measure J/P and bubble point.
- Measure J/P of the module in normal hexane.
- Measure J/P of the module in Durasyn 164 (It is a member of poly-alpha-olefins or PAO's which has same properties as FT wax at ambient conditions)
- Install module in wax loop of the experimental unit.

The following operations were performed during testing with catalyst/wax slurry:

- Expose Scepter modules to catalyst/wax slurry at operating conditions, take samples of initial filtrate and feed tank contents.
- Complete parametric testing
- Send several early samples to TES labs for early determination of filtrate quality.

The following operations were performed after parametric testing was completed:

- Drain wax from wax loop system.
- Rinse wax loop system and module once with used Durasyn 164 and once with virgin Durasyn 164 at 250 ºC (482ºF).
- Move module outside the wax loop experimental unit and wash module with virgin Durasyn 164 at 120ºC (248ºF) and take J/P data in Durasyn 164.
- Wash module two times with normal hexane and take J/P data in hexane.
- Wash module in Ultrasil 91 at 96ºC (205ºF) and water, rinse and take J/P data in water
- Wash module in Dawn dishwashing detergent at 96ºC (205ºF) and water, rinse well and take J/P data in water.
- Wash module in 0.1 molar H3PO4 at 88ºC (190ºF), rinse well and take J/P data in water.

The LCI Scepter filter module used in previous tests for Task 2.3: Fischer Tropsch Catalyst/wax Separation had been exposed to several catalyst mixtures (TES and other LCI clients) and had showed good separation results. For parametric studies it was decided to use a new Scepter module. However, when a new Scepter module with a light application of LCI proprietary

additive powder failed to produce the desired separation efficiency, the test was curtailed pending production of a module with better or similar separation characteristics as obtained with Task 2.3 testing. The probabilities of a successful separation were improved when a 1000 Dalton Membralox® module (M2) operating in parallel with the Scepter module (M1) produced a small quantity of clean filtered wax during the test, suggesting that a smaller opening new Scepter element would be necessary. However, the flux was very low (<1 pound per hour per square foot [lb./h/sf]). In light of the test results, the manufacturer of the Scepter module agreed to supply an alternate Scepter element, with a smaller pore size. Three single-tube modules manufactured by differing techniques were supplied for evaluation and a candidate was chosen. The manufacturer then produced a new 4-tube, 3.8 square feet (sq. ft.) module that was used in the test described herein. A pretreatment of ultra fine LCI proprietary additive powder was applied to the module prior to testing. Parallel to these performance tests, cleaning studies of the fouled elements were performed.

Results

Parametric Tests

Parametric studies of the short-term effects of temperature, operating trans-membrane pressure (TMP), velocity and concentration were performed. Before concentration began, the data were taken at the beginning of the test when the solid concentration was around 1% solids. After the concentration of the wax slurry was completed, at 14 % solids the data were repeated. In addition, at end of concentration period, test filtrate was added back to the concentrated material diluting the feed solids concentration close to the beginning slurry concentration of the test and flux data were taken to evaluate hysterisis effects.

During parametric studies the one parameter of focus was varied through the range of interest while other parameters are held constant. For example when the effect of pressure was evaluated all other parameters such as temperature, velocity and concentration of solids were kept constant while the pressure was changed. This was repeated for other parameters as parameter of focus. The parameter of focus and flux (J) data were taken at several conditions. When variations of a non-focus parameter did occur, corrections were applied to flux data to account for these variations. Below are results from these tests:

Pressure

Figure 2 shows the variation of flux with average TMP pressure for 1 wt % solids slurry and 14 wt % solids slurry at 230°C (446°F) and velocity of 18 feet per sec (FPS). The rate of increase in flux declined as pressure increased. At 1 wt % suspended solids, operating pressures above ~80 pounds per square inch (psi) produced little additional filtrate; at 14 wt % concentration, pressures above ~40 psi produced little increase in flux. Flux seemed to track the same curve whether pressure was being increased or decreased showing little hysterisis effect. The nonlinear effect of pressure (P) on flux is normal in micro-filtration applications. A later figure will show that increasing the axial velocity in the tube can increase the flux at a given pressure.

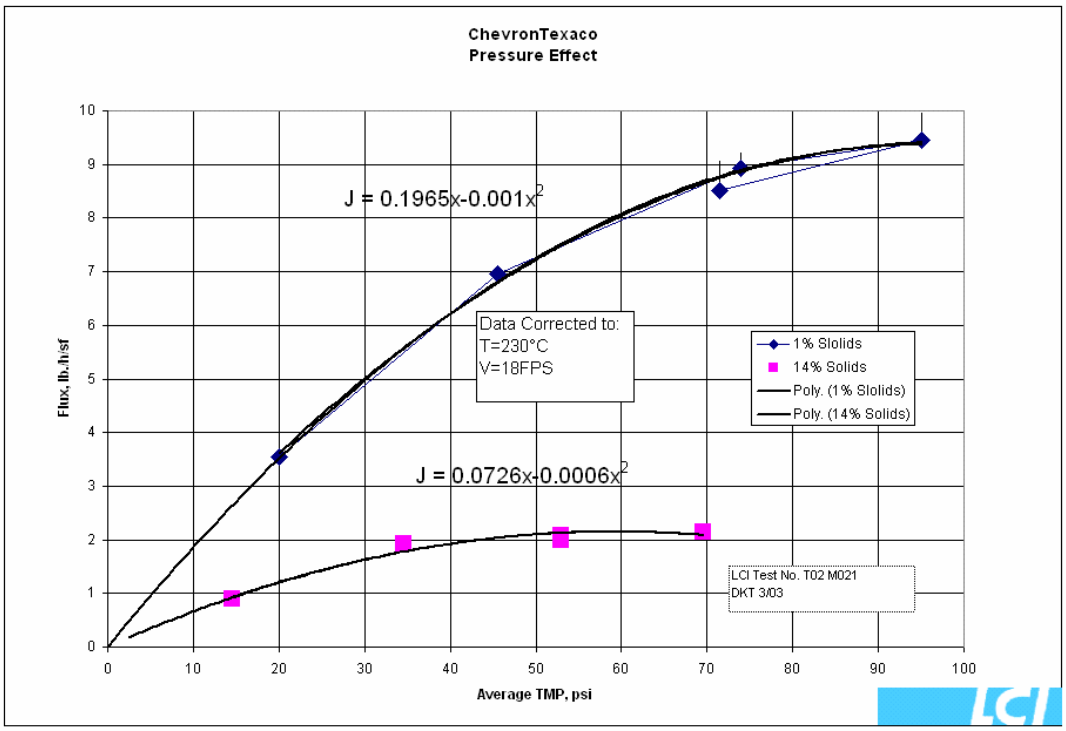


Figure2 Flux vs. Pressure at Two Concentrations

Temperature

Figure 3 shows the variation of flux with inverses of temperature for 1 wt % solids slurry and 14 wt % solids slurry when average pressure TMP is held at 30 psig and velocity is kept constant at 18 FPS. As expected, the logarithm of flux plotted vs. inverse of temperature measured in °Kelvin (°K) resulted in straight-line plots for this material. The slopes of the curves around 503.15°K or 230°C (446°F) imply that a 10°K or 10°C (18°F) increase in temperature results in a 5%-10% increase in flux, depending on suspended solids concentrations.

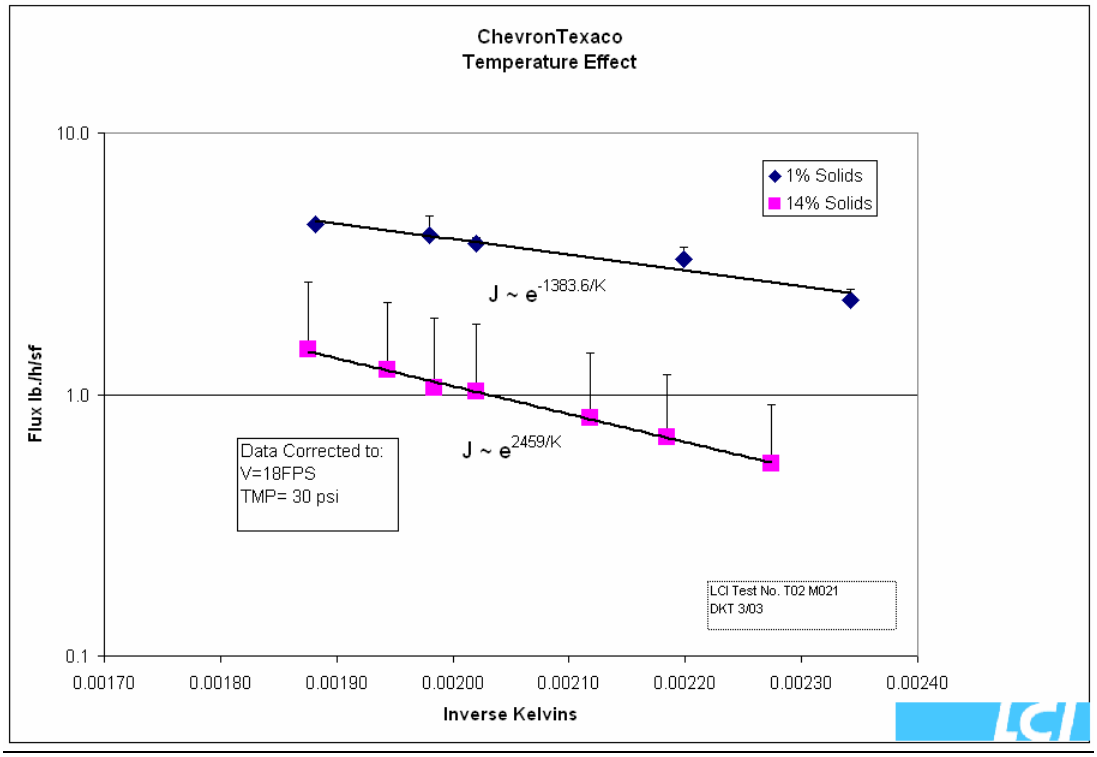


Figure 3. Flux vs. Temperature at Two Concentrations

Velocity

Figure 4 shows the variation of flux with axial velocity for 1 wt % solids slurry and 14 wt % solids slurry when average pressure TMP is held at 30 psig and temperature is held constant at 230 °C(446°F). Like temperature, the effect of axial velocity (V) measured as feet per second (FPS) of fluid velocity on flux was more pronounced at higher concentrations. The effect of velocity on flux is a major variable of consideration because pumping power varies as velocity to the third power.

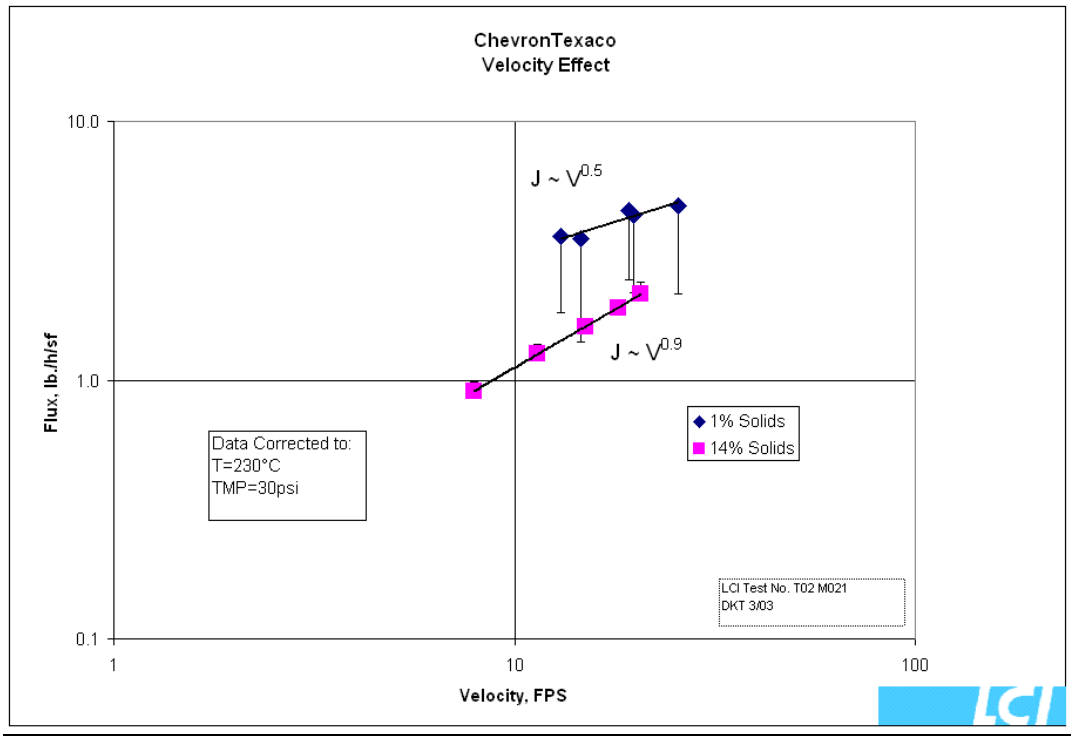


Figure 4. Flux vs. Velocity at Two Concentrations

Concentration

Figure 5 shows the logarithm of flux varying linearly with concentration. Each data series on the plot represents the data from one day as the concentration was increased from 1wt % to 14 wt % in a saw-tooth profile. That is, several dilutions took place during the concentration test as dilute feed was alternately added to the concentrate in the 100 gallon feed tank then filtrate was removed to increase the solids to a new and higher level. This approach was necessary because feed tank capacity was smaller than the feed quantity available for concentration testing. Flux tracked the curve-fit equation on the chart regardless of whether concentration was increasing or decreasing.

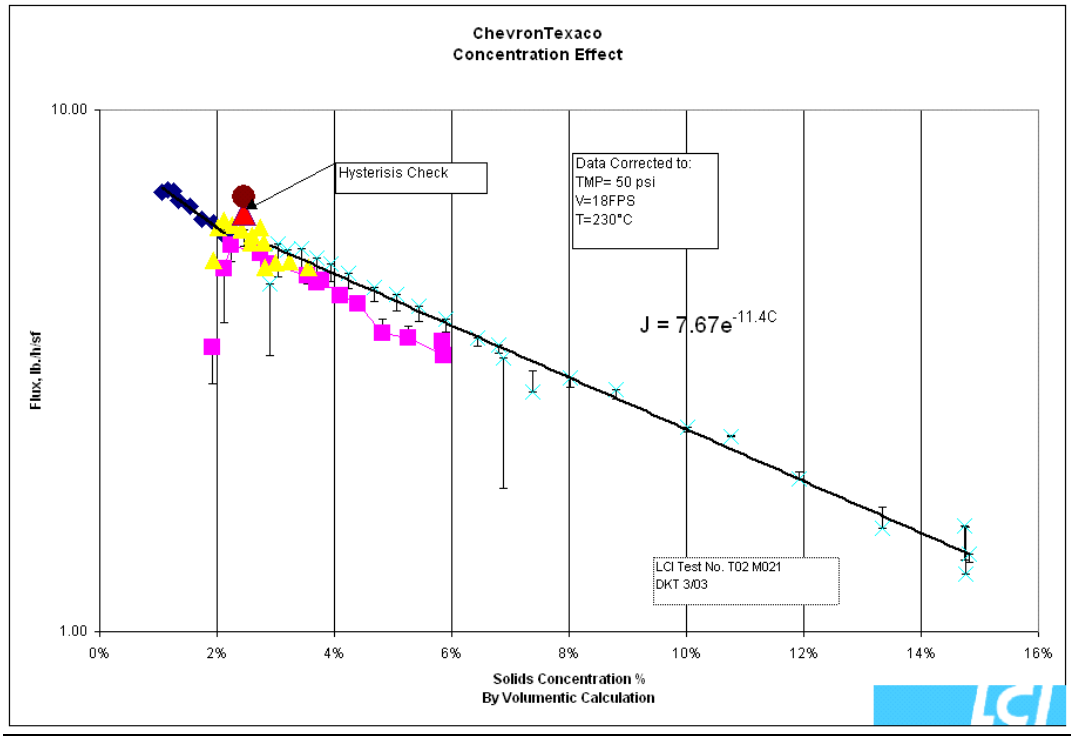


Figure5 . Flux vs. Concentration

Figure 6 shows the same data plotted as was done for Figure 5, this time flux plotted versus volumetric recovery. This presentation shows more clearly the flux with each increment of filtrate removed. By the nature of the process, most filtrate is removed when the flux is relatively high. The last filtrate removed elevates the concentration rapidly. This allows for a multistage design with a smaller last stage.

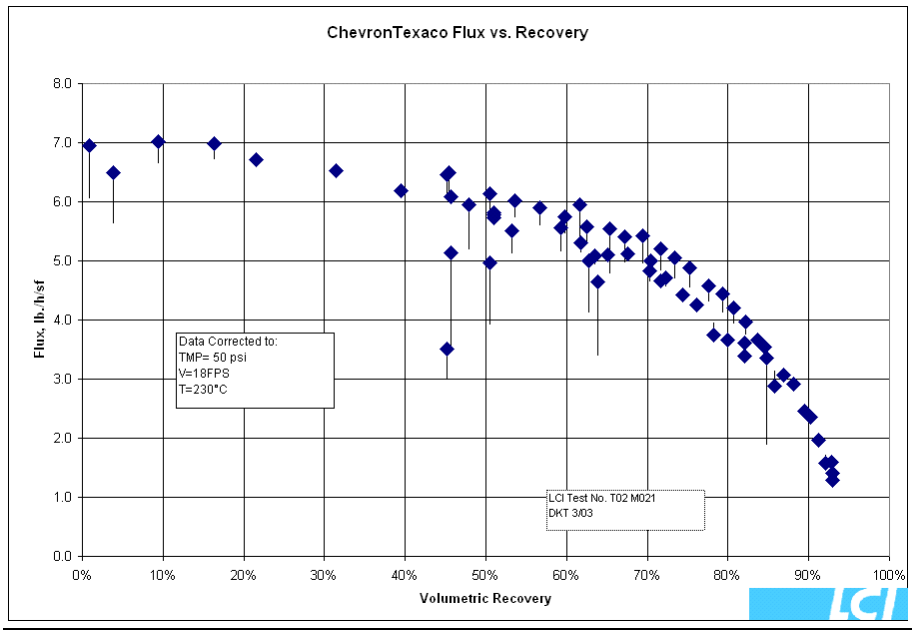


Figure 6 . Flux vs. Recovery

Fouling and Hysterisis

As a simple test for hysterisis, the flux was measured as filtrate was added back to the concentrate to dilute the concentrate from 14 wt % to around 2.5 wt %. The larger circle and triangle in Figure 5 show that the flux tracked up the original concentration curve and displayed practically no hysterisis.

Separation Performance

Table 1 shows the results from the sample analyses performed by TES. All samples show between 2.5 and 3.5 logs of reduction (the logarithm of the ratio of filtrate to feed solids decreased) in suspended solids with higher reductions occurring for the more concentrated feeds. The goal of <10ppm in the filtrate was achieved on two sample taken several hours after startup and stayed at low levels for several test series. Though filtrate solids increased during the test, the solids reduction expressed as the logarithm of the ratio of filtrate to feed solids decreased. Separation efficiency defined as % feed solids removed increased during the test. The filtrate solids concentration will be an integrated value as filtrate at differing concentrations from each stage are mixed to form the composite.

Table 1. Analytical Results

Sample Id	Filtrate, measured as ppm Fe	[2]Slurry, measured as residual solids	[1]Slurry, calculated as ppm Fe	Log reduction
2/26/03 12:10	29.12	1.45%	10,150	-2.5
Duplicate	27.93			-2.6
2/27/03 8:25	5.417	2.20%	15,400	-3.5
2/27/03 14:30	12.1	2.20%	15,400	-3.1
2/28/03 11:30	13.61	3.60%	25,200	-3.3
2/28/03 15:35	7.467	1.91%	13,370	-3.3
3/5/03 9:00	32.81	9.60%	67,200	-3.3
3/5/03 15:10	66.9	18.60%	130,200	-3.3
3/6/03 9:20	67.34	15.30%	107,100	-3.2
3/6/03 11:15	47.23	15.30%	107,100	-3.4
Notes:				
[1]Residual solids assumed to be Fe_2O_3				
[2]Solids determined by burning wax off in open cup, then approximately one hour in an atmospheric furnace at 1600°F.				

Filter Characterizations and Washing Studies

The results of washing studies are presented below in **Figure 7**, which shows characterization parameters for the new filter both prior to and after testing. Ratio of flux to pressure drop (J/P) generally dropped by a factor of 10-100 following testing as shown in the logarithmic presentation. Bubble points following the exposure to the feed stream were greater than 30-psi limit of the test rig in use.

As of this writing, it is not clear whether the lower J/P ratios after testing are due to particle layer buildup on the filter surface or high molecular weight wax (with high melting point) retention in the filter matrix. In future work, employing wax filtrate or virgin, catalyst-free wax as a process fluid at process conditions before and after testing might be a better guide to the particulate layer characteristics.

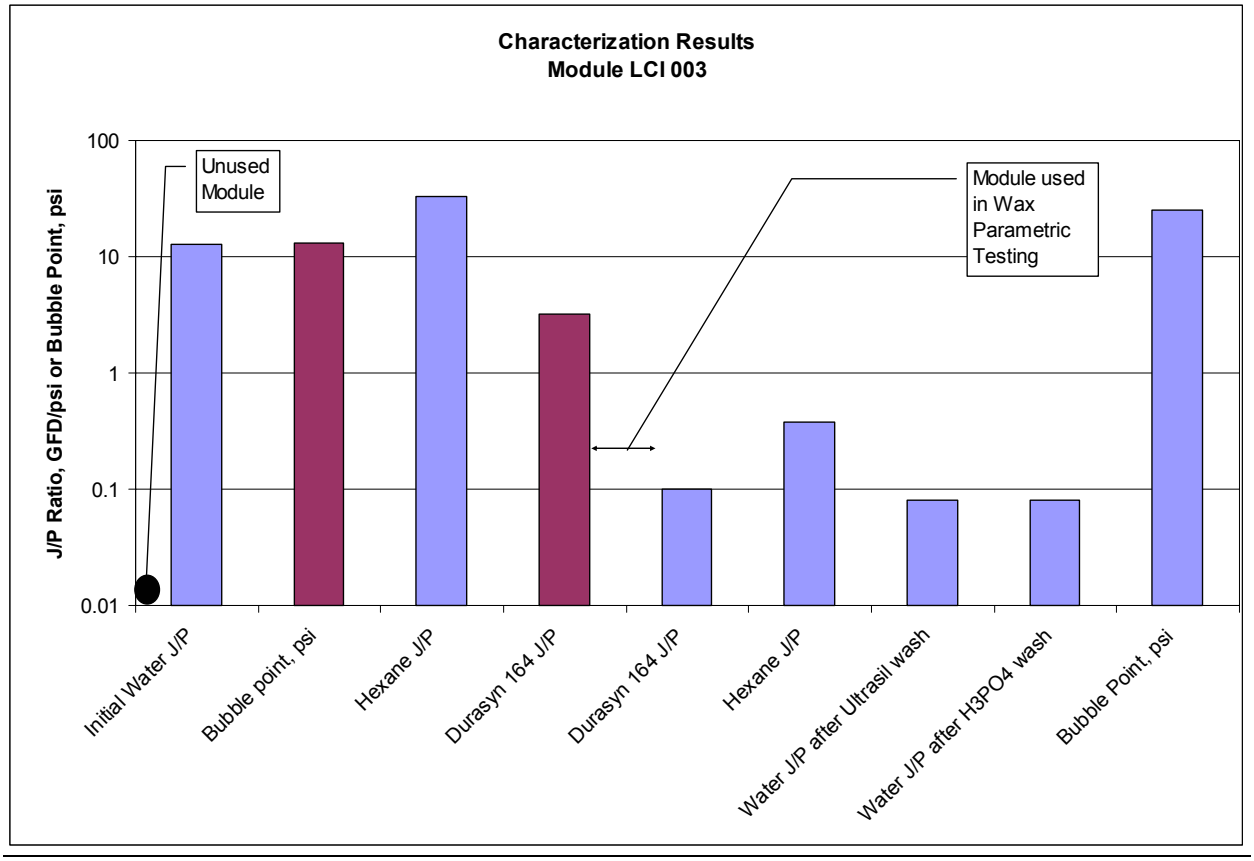


Figure 7. Characterization and Cleaning Results

Conclusions and Recommendations

Conclusions

Filter Performance

Pre-treating the filter element with LCI proprietary additive powder in a water suspension prior to exposure to the feed seemed to reduce the time required to achieve acceptable rejection of the suspended material. While this pretreatment had no measurable effect on the J/P ratio, the bubble point changed from 13 psi to 24 psi. This is consistent with previous observations that the LCI proprietary additive powder serves to block or reduce the size of the largest pores while having little effect on the smaller ones.

Initial J/P ratios measured in Durasyn 164, hexane and water were reflected values expected for unused filters. Measurements following testing showed 1-2 orders of magnitude reduction at the same conditions indicating that a significant resistance layer had developed on the filter surface during testing. Performance during testing showed little hysterisis and steady performance with time, which leads to the conclusion that the resistance layer was formed quickly and then, became stable with little time-related decline during testing. Sometimes a specific feed component present in small quantities causes the majority of the time-dependent fouling. When feed supplies are limited, as they were in this test, the specific component that causes fouling can also be limited leading to a false conclusion about the extent of fouling. Additional performance data with an adequate supply of fresh feed will be needed to determine the long term fouling effects.

Data

Data from this design test were regular, predictable and conformed to expected mathematical forms.

Recommendations

The results of washing study are mixed. The cleaning regimen used following the first, aborted test with these material showed encouraging results. The same regimen after this test yielded very little improvement in standard J/P ratios. Additional work is needed to fine-tune the cleaning procedures to recover fouled filters.

Long-term flux decline information needs to be developed from operation with an adequate supply of fresh feed. Best practice dictates best design data are obtained when tests with fresh feed are scaled to the filter area.

Overall, this test program reduced the risk in the secondary catalyst/wax separation section of the F-T Synthesis Section of the proposed EECP. Task 2.3: Fischer-Tropsch Catalyst/wax Separation identified a successful method for cleaning the F-T wax to less than 10 wppm solids. The RD&T performed for Task 2.3 was a major step in advancing the Rentech F-T Synthesis technology. Based on the results of this task (Task 3.0 Update and Implement Research, Development, and Testing for F-T Catalyst/wax Separation with Micro-filtration), LCI will be able provide the necessary design of a second stage of F-T Catalyst/wax separation system for the EECP.

Bibliography

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Datye, A. K., Shroff, M. D., Jin, Y., Brooks, R P., Wilder, J.A., "Nanoscale attrition during activation of precipitated iron Fischer-Tropsch catalysts: Implications for catalyst design." Department of Energy, 1996.

List of Acronyms and Abbreviations

AFDU	Alternate Fuels Development Unit
AGR	Acid Gas Removal
ASU	Air Separation Unit
BCR	bubble column reactor
CO	carbon monoxide
CO_2	carbon dioxide
FCC	Fluid Catalytic Cracking
F-T	Fischer-Tropsch
F-TPU	Fischer-Tropsch Product Upgrading
Fe	Iron
Fe_2O_3	iron oxide
FPS	feet per second
GE	General Electric
Hz	Hertz
H_2	hydrogen
H_2O	water
H_2S	hydrogen sulfide
HRSG	heat recovery steam generator
J	Flux
J/P	Ratio of flux to pressure drop
K	kelvin
KBR	Kellogg Brown & Root
lb/hr/sqft	pounds per hour per square feet
MDEA	methyldiethanolamine
NOx	nitrogen oxides
P	pressure
Ppmw,PPMW	parts per million (weight)
Ppm,PPM	parts per million
PSI	pound per square inch
RFCC	Resid Fluid Catalytic Cracking
RD&T	Research, Development, and Testing
SF	square feet
SO_2	sulfur dioxide
SQ. FT.	square feet
SRU	sulfur recovery unit
SWS	sour water stripper
TES	Texaco Energy Systems LLC
TMP	trans-membrane pressure
V	velocity
wt%	weight percent